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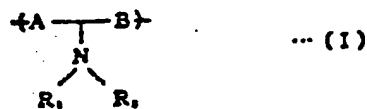
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(54) [Title of the Invention] **Color Migration- and Resoiling Preventive, and Detergent Composition**

(57) [Abstract] (Amended)

5 [Structure] A color migration- and resoiling preventive, comprising a water-soluble polymer with repeating structural units derived from amino group-containing monomers represented by General Formula I etc. or their equivalents, which comprise polymeric products of amino group-containing monomers, or copolymers of such amino group-containing monomers and other monomers that are copolymerizable with such monomers, or equivalents thereof, or subsequently
10 treated products thereof:



15 (where A-B represents a unit constituting the main chain of the polymeric product, the nitrogen N of which is bonded, either directly or by way a methylene group, to either position of A-B, including the A-B terminals; R₁ is a hydrogen, C₁ to C₄ alkyl, alkenyl, or hydroxyalkyl group; and R₂ is a hydrogen, C₁ to C₄ alkyl, alkenyl, or hydroxyalkyl group, where R₁ and R₂ may be
20 joined to form a ring.)

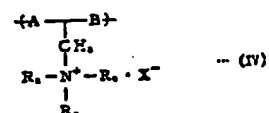
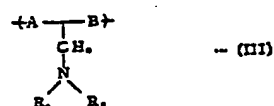
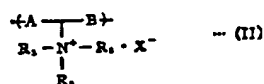
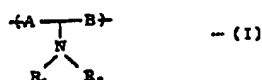
[Effects] The invention effectively prevents color migration and resoiling during laundering, and is also free of iron adsorption such as that encountered with the use of cationic surfactants.

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[Claims]

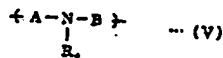
[Claim 1] A color migration- and resoiling preventive, characterized by comprising a water-soluble polymer with repeating structural units derived from amino group-containing monomers represented by General Formulas I, II, and III in Chemical Formula 1 or General Formula V in Chemical Formula 2 or their equivalents, which comprise polymeric products of amino group-containing monomers, or copolymers of such amino group-containing monomers and other monomers that are copolymerizable with such monomers, or equivalents thereof, or subsequently treated products thereof:

[Chemical Formula 1]



(where A-B represents a molecular unit constituting the main chain of the polymeric product, the nitrogen N of which is bonded, either directly or by way a methylene group, to either position of A-B, including the A-B terminals; R₁ is a hydrogen, C₁ to C₄ alkyl, alkenyl, or hydroxyalkyl group; R₂ is a hydrogen, C₁ to C₄ alkyl, alkenyl, or hydroxyalkyl group, where R₁ and R₂ may be joined to form a ring; R₃ is a hydrogen or C₁ to C₄ alkyl, alkenyl, or hydroxyalkyl group; and X is a counterion.);

[Chemical Formula 2]



5

(where A-N-B represents a molecular unit constituting the main chain of the polymeric product, including the nitrogen N, where the nitrogen N may be located at either position of A-B, including the A-B terminals; and R₄ is a hydrogen or C₁ to C₄ alkyl, alkenyl, hydroxyalkyl, or aminoalkyl group).

10

[Claim 2] A detergent composition, characterized by comprising a water-soluble polymer as set forth in Claim 1.

15

[Detailed Description of the Invention]

[0001]

[Field of Industrial Application]

20

The present invention relates to an additive for effectively preventing color migration which has been unavoidable when laundering colored and white clothing at the same time in the same bath, and for also effectively preventing resoiling (which refers to the phenomenon in which soil that has already been removed from clothing adheres again to the clothing and stains it during the laundry process), as well as to a detergent composition comprising such an additive.

25

[0002]

[Prior Art]

A well known problem that needs to be resolved is color migration, which involves the migration of dye from colored clothing to white clothing when these two types of laundry are laundered in the same bath. The problem of color migration has become worse recently because

30

dyeing processes have been simplified in an effort to reduce the cost of clothing, or because of the increase in the availability of imported clothing products which are sometimes characterized by insufficiently developed dyeing techniques.

5 [0003]

Many proposals have been suggested in the past to deal with color migration. One is West German Patent 1,224,698, which discloses the use of cationic surfactants to prevent color migration. However, cationic surfactants cannot be added to most current laundry detergents which are based on anionic surfactants. The use of cationic surfactants results in the problem of
10 resoiling, where soil, particularly oils, which have already been removed during the laundry process remain on the clothing. Another drawback is that the iron in tap water is adsorbed to the clothing.

[0004]

15 Although polyvinyl pyrrolidone (PVP) is known to effectively prevent color migration, no other materials with this effect have been found or put to practical use. This substance also suffers from the drawback of resoiling. Polyvinyl alcohol is presently used for the most part as a resoiling preventive but does not effectively prevent this drawback.

20 [0005]

[Problems Which the Invention Is Intended to Solve]

The present invention is intended to provide an additive which effectively prevents resoiling and color migration without the need to select a particular type of surfactant, as well as a detergent composition comprising such an additive.

25

[0006]

[Means for Solving the Abovementioned Problems]

The color migration- and resoiling preventive of the present invention is characterized by comprising a water-soluble polymer with repeating structural units derived from amino group-
30 containing monomers represented by General Formulas I, II, and III in Chemical Formula 3 or

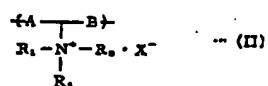
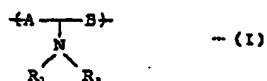
General Formula V in Chemical Formula 4 or their equivalents, which comprise polymeric products of amino group-containing monomers, or copolymers of such amino group-containing monomers and other monomers that are copolymerizable with such monomers, or equivalents thereof, or subsequently treated products thereof:

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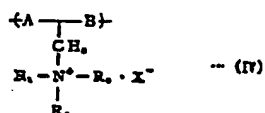
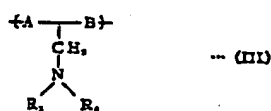
[0007]

[Chemical Formula 3]

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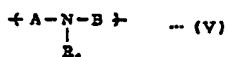
(where A-B represents a molecular unit constituting the main chain of the polymeric product, the nitrogen N of which is bonded, either directly or by way a methylene group, to either position of A-B, including the A-B terminals; R₁ is a hydrogen, C₁ to C₄ alkyl, alkenyl, or hydroxyalkyl group; R₂ is a hydrogen, C₁ to C₄ alkyl, alkenyl, or hydroxyalkyl group, where R₁ and R₂ may be
25 joined to form a ring; R₃ is a hydrogen or C₁ to C₄ alkyl, alkenyl, or hydroxyalkyl group; and X is a counterion.);

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[0008]

[Chemical Formula 4]

5



10 (where A-N-B represents a molecular unit constituting the main chain of the polymeric product, including the nitrogen N, where the nitrogen N may be located at either position of A-B, including the A-B terminals; and R₄ is a hydrogen or C₁ to C₄ alkyl, alkenyl, hydroxyalkyl, or aminoalkyl group).

15 The detergent composition of the present invention is characterized by comprising such a color migration- and resoiling preventive.

[0009]

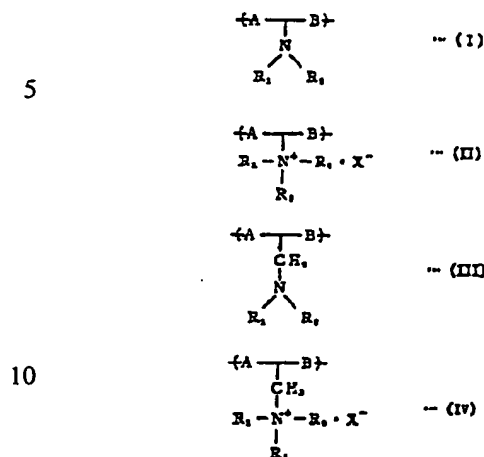
[Embodiments of the Invention]

20 The color migration- and resoiling preventive of the present invention comprises a water-soluble polymer typically obtained by the polymerization of an amino group-containing monomer. Examples of the mode of polymerization include addition polymerization typical of vinyl monomers and polycondensation typical of amino acid monomers. Amino group-containing monomers can be obtained directly by polymerization, or structural units represented by General Formulas 1 through IV in Chemical Formula 5 or General Formula V in Chemical
25 Formula 6 below can be introduced into the polymeric product by means of polymerization and subsequent post-treatment.

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[0010]

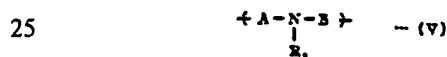
[Chemical Formula 5]



(where A-B represents a molecular unit constituting the main chain of the polymeric product, the nitrogen N of which is bonded, either directly or by way a methylene group, to either position of A-B, including the A-B terminals; R₁ is a hydrogen, C₁ to C₄ alkyl, alkenyl, or hydroxyalkyl group; R₂ is a hydrogen, C₁ to C₄ alkyl, alkenyl, or hydroxyalkyl group, where R₁ and R₂ may be joined to form a ring; R₃ is a hydrogen or C₁ to C₄ alkyl, alkenyl, or hydroxyalkyl group; and X is a counterion);

20 [0011]

[Chemical Formula]



(where A-N-B represents a molecular unit constituting the main chain of the polymeric product, including the nitrogen N, where the nitrogen N may be located at either position of A-B,

including the A-B terminals; and R_4 is a hydrogen or C_1 to C_4 alkyl, alkenyl, hydroxyalkyl, or aminoalkyl group).

[0012]

The aforementioned General Formula II represents a salt or quaternary ammonium compound of General Formula I, where the salt (counterion) is typically a hydrochloride (chloride). General Formula IV represents a salt or quaternary ammonium compound of General Formula III, where the salt (counterion) is typically a hydrochloride (chloride).

[0013]

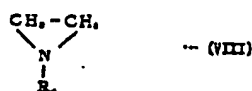
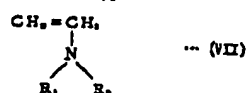
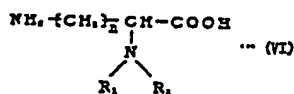
The hydroxyalkyl groups in the aforementioned general formulas can be introduced by the addition of an alkylene oxide to nitrogens with active hydrogen. The mean number of mols added is not particularly limited but is preferably 1 to 3 mols.

[0014]

Specific examples of amino group-containing monomers typically include the monomers represented by the following General Formulas VI and VII in Chemical Formula 7 below or their quaternary ammonium compounds, intramolecular dehydrated cyclic compounds of General Formula VI, ethyleneimines of General Formula VIII, and other derivatives.

[0015]

[Chemical Formula 7]



(where n is an integer of 0 to 8; R₁ is a hydrogen, C₁ to C₄ alkyl, alkenyl, or hydroxyalkyl group; R₂ is a hydrogen, C₁ to C₄ alkyl, alkenyl, or hydroxyalkyl group, where R₁ and R₂ may be joined to form a ring; and R₄ is a hydrogen or C₁ to C₄ alkyl, alkenyl, hydroxyalkyl, or alkenyl [sic] group).

[0016]

General Formula VI is an α -amino acid such as aminocaproic acid where n=4. In ϵ -caprolactam, the terminal amino group and carboxylic acid are bonded (dehydrated) to form a ring. Such amino acid monomers form water-soluble polymers through polycondensation.

[0017]

In General Formula VI, n is an integer of 0 to 8, and preferably 2 to 5. R₁ and R₂ are each independently a hydrogen or C₁ to C₄ alkyl, alkenyl, or hydroxyalkyl group, and are each preferably a hydrogen, methyl, ethyl, hydroxyethyl, or hydroxypropyl. Specific examples of R₁/R₂ include H/H, H/CH₃, CH₃/CH₃, etc.

[0018]

General Formula VII represents aminoethylenes (vinylamines), where R₁ and R₂ are each independently a hydrogen or C₁ to C₄ alkyl, alkenyl, or hydroxyalkyl group, and are each preferably a hydrogen, methyl, or ethyl. Specific examples of R₁/R₂ include H/H, H/CH₃, CH₃/CH₃, etc.

[0019]

General Formula VII includes aminoethylenes (=vinylamines) in which R₁ and R₂ are both hydrogen, but vinylamines are not known in the form of monomers. Vinylamine units can accordingly be introduced into polymeric products by polymerization using such derivatives, followed by post-treatment. Specifically, they are polymerized in the form of derivatives N-substituted with ethyl carboxylates (diethyl vinylamine-N,N-dicarboxylates), and are hydrolyzed following polymerization to introduce the vinylamine-derived structural units into the polymeric product.

[0020]

In addition, following the radical polymerization of N-vinylformamide, aminoethylene-derived structural units can be introduced by means of hydrolysis with an acid or base.

5 [0021]

General Formula VIII more effectively prevents color migration when a polyethyleneimine or derivative is formed by ring-opening polymerization, and R₄ bonded to the nitrogen N is substituted rather than being hydrogen. When R₄ bonded to nitrogen is hydrogen, the hydrogen is active hydrogen and can be substituted by the addition of a hydroxyalkyl group
10 such as hydroxyethyl or hydroxypropyl by post-treatment with a hydroxyalkylene. Such vinyl monomers can form water-soluble polymers through polycondensation.

[0022]

The water-soluble polymer of the present invention may be a homopolymer of an amino
15 group-containing monomer such as the above, or a copolymer of two or more amino group-containing monomers, and may also be a copolymer of at least one amino group-containing monomer and another monomer that is copolymerizable with such a monomer.

[0023]

20 Examples of other copolymerizable monomers include addition polymerized monomers such as ethylene, vinyl pyrrolidone, acrylic acid, acrylamide, vinyl alcohol, allyl alcohol, vinyl benzenesulfonate, and vinyl benzenecarboxylic acids.

[0024]

25 For example, polyethylenes that are aminoated following polymerization are the equivalent of copolymers of aminoethylene units and ethylene units, and have the same action and effects as the invention. As the equivalent of the invention, they are included in the scope of the claims. Aminoated polypropylenes are the equivalent of polyallylamine or allylamine and propylene copolymers.

30

[0025]

The extent of aminoation can be determined and controlled by titration (where percentages are checked by neutral titration), IR spectroscopy, NMR-based determination of structural percentages, and colorimetric quantification for preparing dyes with coupling reagents and nitrous acid.

[0026]

Examples of other monomers copolymerizable by polycondensation include aminocarboxylic acids represented by General Formula IX in Chemical Formula 8 below, glutamic acid, alginic acid, and similar amino acids.

[0027]

[Chemical Formula 8]



(n: integer of 0 to 9)

[0028]

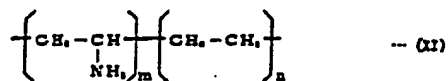
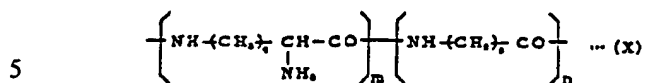
The copolymer of (a) an amino group-containing monomer and (b) another monomer used in the present invention has a molar weight ratio a/b of 100/0 to 50/50, preferably a ratio a/b of 100/0 to 70/30, and even more preferably 100/0 to 80/20.

[0029]

Typical examples of copolymers or homopolymers (m/n = 100/0) in the present invention include water-soluble nylons represented by General Formula X in Chemical Formula 9 below (AQ Nylon and the like by Toray), polyethyleneamines of General Formula XI, polyallylamines of General Formula XII in Chemical Formula 10 below, and polydiallyldimethylammonium chlorides of General Formula XIV.

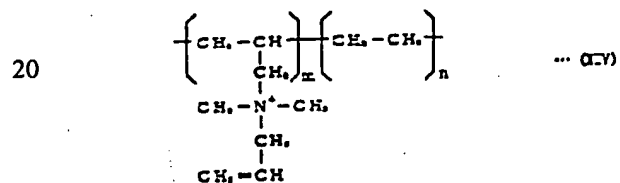
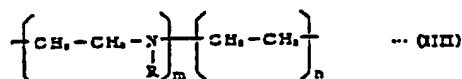
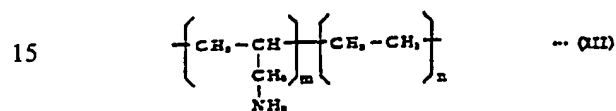
[0030]

[Chemical Formula 9]



10 [0031]

[Chemical Formula 10]



25 [0032]

Any of General Formulas X, XI, XII, XIII, and XIV preferably have a polymerization ratio m/n of 100/0 to 50/50, more preferably 100/0 to 70/30, and even more preferably 100/0 to 80/20. In General Formula XIII, R is a hydroxyethyl, hydroxypropyl, or the like.

30

[0033]

Polyethyleneamines or hydrolyzable nylons and the like can be used to form salts such as hydrochlorides. It is important for the polymeric product of the present invention to be water-soluble. The effects of the present invention cannot be achieved if the polymeric product has amino group-containing structural units yet is not water-soluble.

[0034]

The water-soluble polymer of the present invention should have a weight-average molecular weight of between 150 and 5,000,000, and preferably between 500 and 1,000,000.

The color migration- and resoiling preventive of the present invention may be made in the form of a preparation by itself and used separately with a detergent composition at the time of use. It may also be blended in a prescribed amount with a detergent composition in the form of a detergent composition for preventing color migration and resoiling (the detergent composition of the present invention).

[0035]

The detergent composition of the present invention can contain a surfactant, builder, and other detergent compositions.

[0036]

Examples of anionic surfactants include the following:

1) Linear alkylbenzenesulfonates containing alkyl groups with a mean carbon number of 8 to 16

2) α -olefinsulfonates with a mean carbon number of 10 to 20

3) fatty acid lower alkyl ester sulfonates with fatty acid residue having a carbon number of 8 to 22

[0037]

4) alkylsulfates with a mean carbon number of 10 to 20

5) alkyl ether sulfates or alkenyl ether sulfates with straight-chain or branched alkyl groups or alkenyl groups with a mean carbon number of 10 to 20, and ethylene oxide added in an average of 0.5 to 8 mols

6) saturated or unsaturated fatty acid salts with a mean carbon number of 10 to 22

10

The counterions of such anionic surfactants are preferably alkali metal salts such as sodium or potassium.

[0038]

15 The following are examples of nonionic surfactants.

1) EO adduct nonionic surfactants comprising an average of 6 to 25 mols ethylene oxide (EO) added to C₈ to C₁₈ primary or secondary alcohols (alkyl ether ethoxylates)

20 [0039]

2) EO-PO adduct nonionic surfactants comprising an average of 10 to 25 mols ethylene oxide (EO) and 1 to 10 mols propylene oxide (PO) added to C₈ to C₁₈ primary or secondary alcohols

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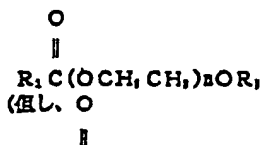
3) fatty acid polyoxyethylene alkyl ethers represented by Chemical Formula 6 [sic]

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[0040]

[Chemical Formula 11]

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R₁C: C₈ to C₁₈ fatty acid residue

10 (n: number of mols of ethylene oxide added (mean of 5 to 30))

R₂: C₁ to C₅ alkyl group)

[0041]

15 Such nonionic surfactants are alkyl ethers of ethylene oxide adducts of fatty acids comprising ethylene oxide added between ester linkages. These are obtained in two stages by the addition of ethylene oxide to fatty acids by a common method and subsequent alkyl ether conversion. They can also be produced by a single stage method, for example, by bringing about a reaction between ethylene oxide and a fatty acid alkyl ester in the presence of a catalyst
20 consisting of magnesium oxide containing one or more metallic ions selected from trivalent aluminum ions, gallium ions, indium ions, thallium ions or the like, and divalent manganese ions (Japanese Unexamined Patent Application (Kokai) 4-279552).

[0042]

25

4) sugar ester nonionic surfactants consisting of esters of C₆ to C₁₈ fatty acids and C₃ to C₆ monosaccharides or their monoalkyl ethers

5) Sugar alkyl ether nonionic surfactants represented by Chemical Formula 7 [sic]

30

[0043]

[Chemical Formula 12]



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R_1 : C_8 to C_{18} alkyl groups; n : 0 to 12; Z : C_5 to C_6 sugar residues; x : 1.2 to 10)

[0044]

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6) C_8 to C_{18} fatty acid alkanolamides

7) alkyl (C_8 to C_{18}) dimethylamine oxides

[0045]

15

Examples of builders and other detergent components include inorganic builders such as sodium tripolyphosphate or sodium pyrophosphate; calcium ion-sequestering builders such as aluminosilicates (zeolites), sodium citrate, sodium ethylenediamine tetraacetate, nitrilotriacetates, sodium polyacrylates, sodium acrylate-anhydrous sodium maleate copolymers, and polyacetal carboxylates; alkaline builders such as sodium carbonate, potassium carbonate, and silicates; sulfites and sulfates; resoiling preventives such as polyethylene glycol; enzymes such as proteases, lipases, cellulases, and amylases; softeners such as quaternary ammonium salts and bentonites; and bleaches, whiteners, fragrances, and dyes. The detergent composition of the present invention should contain the color migration- and resoiling preventive of the present invention in an amount of between 0.1 and 10 wt%, and preferably between 0.5 and 5 wt%.

25

[0046]

[Effects of the Invention]

The present invention allows the problems of color migration and resoiling to be prevented during laundering, and is also free of iron adsorption commonly encountered with the use of cationic surfactants.

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[0047]

[Examples]

The effects of the present invention are described in greater detail below with reference to examples. The methods of evaluation used in the examples are discussed first. The following
5 dyed fabrics and white fabrics were used in the color migration and resoiling tests.

[0048] 1) Dyed Fabric

The standard dyed fabric used was cotton (knitted) dyed with blue reactive dye Sumifix
10 Supra (by Sumitomo Kagaku) (Blue BRF CI reactive Blue 221). These were dyed at a dye concentration of 4% (owf.).

[0049] 2) White Fabric

15 The white fabric used was Petrochemical Association fabric (test fabric indicated by the Petrochemical Association) (polyester jersey was simultaneously used during resoiling tests). These test fabrics were used in the color migration and resoiling tests.

[0050] 1. Color Migration Test

20

Based on consumer claims about color migration, the tests were run for 1 hour at 40°C at an additive concentration of 500 ppm (detergent concentration 5000 ppm when used with detergent), and a 20-fold bath ratio (100 g dyed fabric + 10 g white fabric + 140 g other cotton fabric/5 L detergent solution). Following the conclusion of the above, the white color migration
25 test fabric was rinsed for 3 minutes in 30 L of 25°C water, dehydrated, dried using an iron, and then visually inspected (evaluated by blueness).

	Rating	Criteria
30	A	no migration

B	slight migration
C	evident migration
D	considerable migration

5 [0051] 2. Resoiling Test

Soiled white shirts were used to assess resoiling. The tests were run for 10 minutes at 25°C, a detergent concentration of 833 ppm (standard concentration), and a 30-fold bath ratio (resoiling test fabric (10 g cotton, 10 g polyester) + undershirt 980 g/30 L detergent solution).

10 Following the conclusion of the above, the resoiling test fabric was rinsed for 3 minutes, dehydrated, dried using an iron, and then visually inspected (based on darkening).

	Rating	Criteria
15	A	no resoiling
	B	slight resoiling
	C	evident resoiling
	D	considerable resoiling

20 [0052] Examples

Water-soluble polymers consisting of the polymers given in Table 1 were used in evaluations of color migration and resoiling, with the results given in the same table. The detergent used was a commercially available detergent consisting of the following composition
25 (by weight).

	α -sulfofatty acid methyl ester, sodium	10%
	sodium α -olefinsulfonate	5%
	linear sodium alkylbenzenesulfonate	10%
30	zeolite	25%

carbonate	40%
nonionic surfactant	5%
enzyme	2%
fluorescent whitener, moisture, etc.	balance

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[0053]

The α -amino- ϵ -caprolactam/ ϵ -caprolactam used in the table was AQ Nylon by Toray, the polyethyleneimine and derivatives were samples from Nihon Shokubai, and the other ingredients were synthesized. These polymeric products were completely water-soluble at the

10 concentrations used.

[0054]

The ethyleneamine and vinyl alcohol units were polymerized using the respective precursors, and were hydrolyzed following polymerization to introduce the ethyleneamine units

15 and vinyl alcohol units in the form of repeating units into the polymeric substances.

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[0055]

[Table 1]

Table 1: Types of water-soluble polymers, and results of evaluation

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Sample No.	Polymer	Results of evaluation		
		Color migration		Resoiling
		Polymer aqueous solution	Detergent system	Detergent system
1*1	PVA	D	D	B
2*1	PAA-Na	D	D	B
3	Am ϵ Cp/ ϵ Cp (50/50)	B	C	B
4	Am ϵ Cp/ ϵ Cp (70/30)	A	B	A
5	Am ϵ Cp/ ϵ Cp (80/20)	A	B	A
6	PAm ϵ Cp	A	A	A
7	dMeAm ϵ Cp/ ϵ Cp (80/20)	A	A	A
8	Am ϵ Cp/Glc (80/20)	A	A	A
9	Am ϵ Cp/Glt (80/20)	A	A	A
10	Am ϵ Cp/Arg (80/20)	A	A	A
11	AmEt/Et (80/20)	B	B	A
12	PAmEt	A	A	A
13	AmEt/VA (80/20)	A	A	A
14	AmEt/AA-Na (80/20)	A	A	A
15	PA1Am	A	B	B
16	PA1AM-HCl	B	B	B
17	PdAldMeAm-Cl	A	A	B
18	PEtIm	B	B	B
19	PEtIm-HEt	A	A	A
20	PEtIm-HPPr	A	A	A

*1) Sample Nos. 1 and 2 are a comparative example and another example

PVA: polyvinyl alcohol

PAA-Na: sodium polyacrylate

Am ϵ Cp/ ϵ Cp (50/50): α -amino- ϵ -caprolactam/ ϵ -caprolactam copolymer – parentheses indicate copolymer ratio (same below)

5 PAm ϵ Cp: poly α -amino- ϵ -caprolactam

dMeAm ϵ Cp/ ϵ Cp (80/20): α -dimethylamino- ϵ -caprolactam/ ϵ -caprolactam copolymer

Am ϵ Cp/Glc (80/20): α -amino- ϵ -caprolactam/glycine copolymer

Am ϵ Cp/Glt (80/20): α -amino- ϵ -caprolactam/glutamic acid copolymer

Am ϵ Cp/Arg (80/20): α -amino- ϵ -caprolactam/arginine copolymer

10 AmEt/Et (80/20): aminoethylene/ethylene copolymer

PAmEt: polyaminoethylene

AmEt/VA (80/20): aminoethylene/vinyl alcohol copolymer

AmEt/AA-Na (80/20): aminoethylene/sodium acrylate copolymer

PA1Am: polyallylamine

15 PA1AM·HCl: polyallylamine hydrochloride

PdAldMeAm·Cl: polydiallyldimethylammonium chloride

PEtIm: polyethyleneimine

PEtIm·HEt: polyethyleneimine-hydroxyethyl adduct

PEtIm·HPr: polyethyleneimine-hydroxypropyl adduct

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